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Study of Thermal Sensitivity and Thermal Explosion Violence of Energetic Materials in the LLNL ODTX System

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Abstract. Incidents caused by fire and combat operations can heat energetic materials that may lead to thermal explosion and result in structural damage and casualty. Some explosives may thermally explode at fairly low temperatures (< 100 C) and the violence from thermal explosion may cause a significant damage. Thus it is important to understand the response of energetic materials to thermal insults. The One Dimensional Time to Explosion (ODTX) system at the Lawrence Livermore National Laboratory has been used for decades to measure times to explosion, threshold thermal explosion temperature, and determine kinetic parameters of energetic materials. Samples of different configurations (pressed part, powder, paste, and liquid) can be tested in the system. The ODTX testing can also provide useful data for assessing the thermal explosion violence of energetic materials. Recent ODTX experimental data are reported in the paper.

1. Introduction

Accidents involving with thermal explosion (or cook-off) of energetic materials are costly. Over the last few decades, there has been considerable research effort on the thermal decomposition and thermal explosion violence of energetic materials at elevated temperatures in different sample geometries and confinement [1-3]. Thermal explosion studies on various energetic materials in two-dimensional geometry such as the Scaled-Thermal-Explosion-Experiment (STEX) system [4] and the Sandia-Instrumented-Thermal-Ignition (SITI) system have been reported [5]. The One Dimensional Time to Explosion (ODTX) system at the Lawrence Livermore National Laboratory (LLNL) has been used since 1970s for cook-off study [6-10]. It is attractive because of the one-dimensional geometry, providing a minimal sample requirement (up to 2 grams for each test) and low cost. The ODTX testing generates three technical data: (1) lowest temperature at which thermal explosion would occur (threshold temperature, T_{li}); (2) times to thermal explosion at temperatures above T_{li} for the calculation of activation energy and frequency factor; and (3) thermal explosion violence.

2. System Description and Experiments

The ODTX system, as shown in Figure 1, is operated remotely in a test cell. The testing involves heating a 1.27-cm diameter spherical sample in a spherical cavity between two aluminum anvils. The sample is remotely delivered to the anvil cavity via the sample delivery system when the anvils reach a

predetermined temperature. A microphone sensor measures a sound signal, which indicates the time at which a thermal explosion occurs. The detail description of the LLNL ODTX system can be found elsewhere [11].

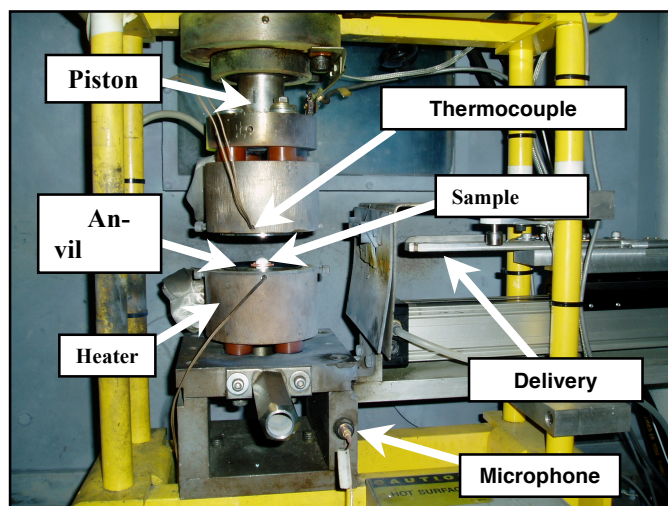


Figure 1. LLNL ODTX system

Samples of various configurations (pressed parts, cast parts, powders, pastes, and liquids) can be tested in the ODTX system. Pressed and cast samples are loaded into the cavity of aluminum anvils directly without secondary containment. An aluminum shell is used as a secondary containment to hold powder samples, pasty samples, or liquid samples before loading to the system. ODTX tests are typically run 10 to 20 times at various temperatures to obtain time to thermal explosion charts. The tests require a total of 30 grams of material. Figure 2 shows typical ODTX test data for several high explosives: TATB, TNT, HMX, RDX and PETN.

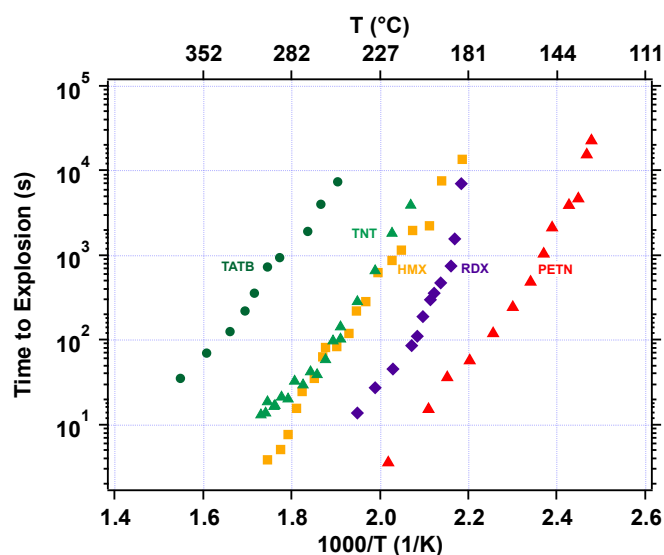


Figure 2. Times to thermal explosion at different temperatures for various high explosives. PETN is much more thermally sensitive than RDX, HMX, and TATB.

3. Recent Experimental Results

3.1 Thermal sensitivity of energetic liquid mixtures

Highly concentrated hydrogen peroxide (HP) is widely known as a powerful oxidizer, and, when mixed with fuel, may produce a powerful explosive mixture. Understanding the response of HP/fuel mixtures to heat is paramount for their safe handling and storage. Several HP/fuel mixtures were formulated and tested in the ODTX system with the results shown in Figure 3. All of these liquid mixtures were more sensitive to thermal explosion than PETN, with some that thermally exploded at temperatures less than 80 C. Table 1 shows the lowest temperatures at which thermal explosion (threshold temperature, T_{li}) would occur. The seven HP/fuel liquid mixtures we have tested showed all had T_{li} lower than some commonly used high explosives.

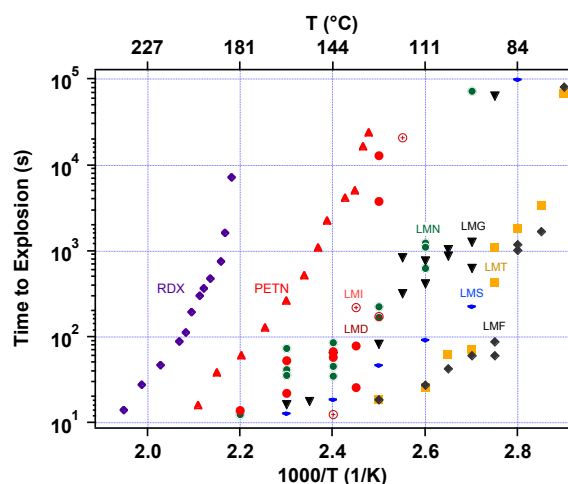


Figure 3. ODTX results of several liquid explosives.

Table 1. T_{li} for H_2O_2 /fuel mixtures [12, 13]. The liquid samples were confined in a 1.27-cm diameter spherical aluminium shell

Energetic HP/fuel liquid mixtures	T_{li} , °C
LMF (HP/Fructose)	71.7
LMT (HP/Drink mix)	71.7
LMS (HP/Sugar)	84.0
LMG (HP/Glycerol)	90.5
LMN (HP/Nitromethane)	97.2
LMD (HP/Diesel)	111.5
LMI (HP/Isopropanol)	119.0
PETN	130.0
HMX	180.0
TATB	230.0

3.2. Thermal explosion violence of energetic liquid mixtures

Figure 4 shows the anvils before and after the thermal explosion of HP/glycerol. The anvils indicated some melting from the extremely hot gas generated by the explosion. The blast energy (energy of explosion) from the thermal explosion can be estimated from the crater size in the aluminum anvils [3, 11]. A surface profilometer was used to measure the increase in crater volume after the blast. The av-

average increases in crater volumes for HP/glycerol and HP/IPA were 0.53 cc and 0.65 cc, respectively, which is less than 1.52 cc, the average crater volume increase by LX-04 (an HMX-based formulation). The average crater volume increases for the seven HP/fuel mixtures tested were all significantly less than that for HMX-based formulations.

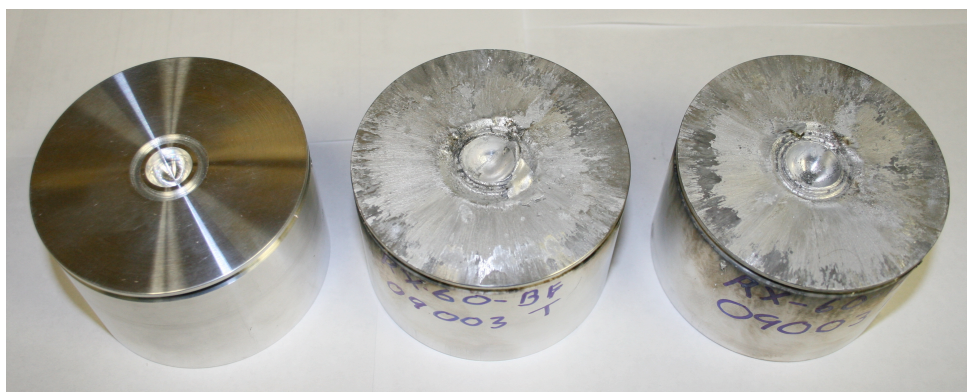


Figure 4. Anvils before and after thermal explosion of HP/glycerol; left was the pristine anvil; also shown are top anvil (middle) and bottom anvil (right) after the thermal explosion.

3.3 ODTX Data modeling for energetic liquid mixtures

The times to explosion data for the HP/fuel mixtures can be modeled to obtain their thermal decomposition kinetic parameters, as represented by a single-step Prout-Tompkins (Arrhenius) equation [12-13].

$$\frac{dx}{dt} = -A \exp\left(-\frac{E}{RT}\right) x^n (1 - qx)^m \quad (1)$$

Where

x = mass fraction of reactant remaining, dimensionless

A = frequency factor, second^{-1}

E = the activation energy, J/mole

R = universal gas constant, $8.314 \text{ J}/(\text{°K} \cdot \text{mol})$

T = temperature, K

n, m, q = Prout-Tompkins model kinetics parameters, dimensionless

Eq (1) becomes a first order Arrhenius rate when $m = 0$ and $n = 1$. We use a first order Arrhenius rate in this work. The parameters in the above models were adjusted to fit measurements of the One-Dimensional-Time-to-Explosion (ODTX) as described above. Figure 5 shows the ODTX data modeling for HP/sugar mixture with kinetic labelled.

This approach has been applied successfully to many high explosives. In this case, the model is applied to the HP/fuel mixtures to determine kinetic parameters A and E . Table 2 lists chemical kinetics parameter for decomposition of HP mixtures. All rates are first order Arrhenius kinetics.

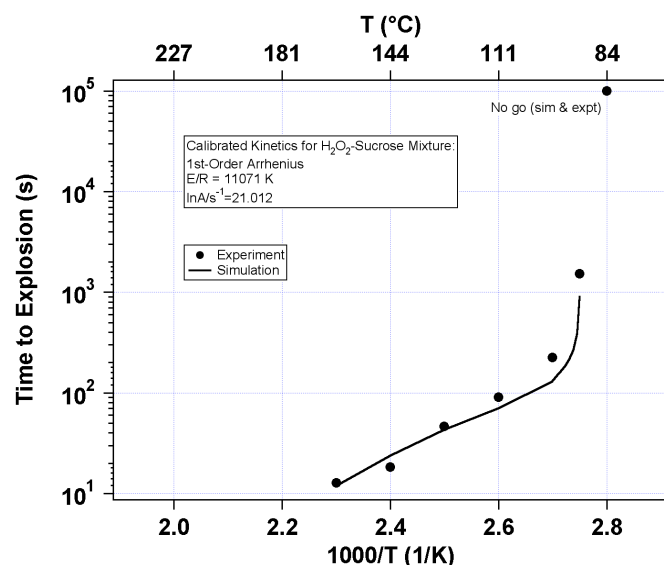


Figure 5. ODTX experimental results and model for HP/sugar (sucrose) mixture.

Table 2. Chemical kinetics parameter for decomposition of HP mixtures. All rates are first order Arrhenius kinetics

Parameter	HP/diesel	HP/fructose	HP/glycerol	HP/Isopropanol	HP/sugar	HP/drink mix
$\ln(A), s^{-1}$	33.779	29.926	24.896	98.134	21.012	30.156
$E/R, 1/^{\circ}K$	17459	13956	12773	42701	11071	14039
m	0	0	0	0	0	0
n	1.0	1.0	1	1.0	1.0	1.0

3.4 Thermal sensitivity data for new energetic molecules LLM-191 and DAAF

The ODTX system is currently being used for IHE (insensitive explosive) qualification test for thermal sensitivity and thermal explosion violence. It is also a tool for cook-study on new energetic materials. We recently conducted ODTX tests on two new molecules LLM-191 and DAAF and the results are shown in Figure 6 and Figure 7, respectively. LLM-191 [(3,5-bis(4-nitro-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazole)] is a new energetic molecule recently made at LLNL with a low melting point (61 C). With a density of 1.9 g/cc (15% higher than TNT), and a detonation velocity of 8,600 m/s (25% higher than TNT), LLM-191 is a candidate for melt-castable explosive. The ODTX tests show a unique thermal sensitivity profile. At high temperature region (> 230 C), its thermal sensitivity is similar to that of TNT. At lower temperature region (< 230 C), its thermal sensitivity is similar to that of TATB. Its threshold temperature for thermal explosion is 230 C (same as TATB), and much higher than those of TNT, HMX, RDX and PETN.

DAAF (3,3'-diamino 4,4'-azoxyfuran) was first synthesized at Los Alamos National Laboratory in 1981, was tested in the ODTX system in 1997, 2006, and 2010, respectively, with different results. Samples tested in 1997 were quite thermally sensitive, due to the presence of some thermally sensitive impurities. Subsequent ODTX tests in 2006 and 2010 on pure DAAF samples show marked improvements in thermal sensitivity. DAAF from 1997 behaved similarly to PETN as opposed to DAAF 2006, which behaved similarly to HMX and TNT. Test data for DAAF were more scattered than with other conventional high explosives.

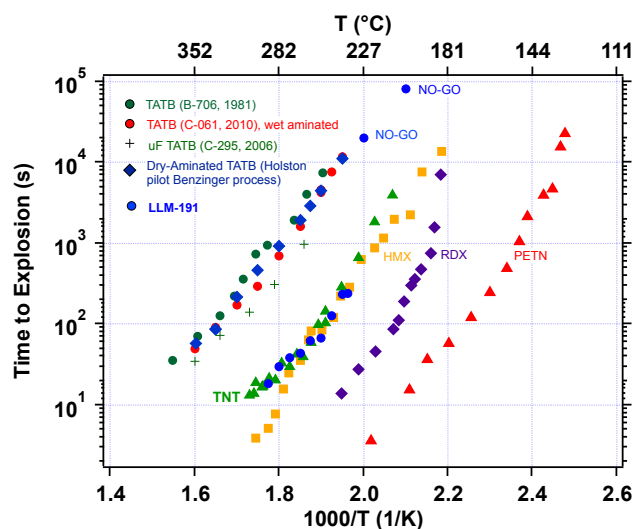


Figure 6. Times to thermal explosion at different temperatures for LLM-191.

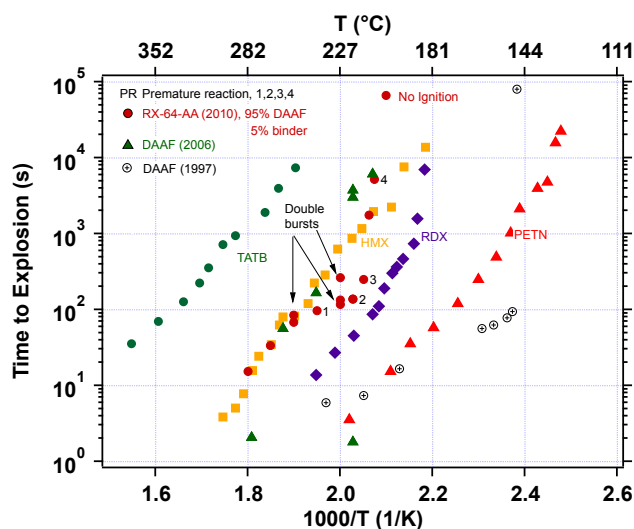


Figure 7. Times to thermal explosion at different temperatures for DAAF tested in 1997, 2006, and 2010.

2. Summary and conclusions The ODTX system is being used for the IHE qualification test as well as for the measurements of thermal sensitivity, thermal decomposition kinetic parameters, and thermal explosion violence. Samples in various configurations can be tested. Most of energetic liquids we have tested in the ODTX system showed low threshold temperatures (as low as 80 °C) for thermal explosion to occur. Test result also showed that LLM-191 is fairly thermally stable and may be a good candidate molecule for melted-cast formulations. In summary, the ODTX system is a useful tool for cook-off study due to its relatively low cost and low requirement of material (30 grams).

3. Acknowledgments

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